MICROBIAL RESIDUAL BIOMASS AS BIOSORBENT FOR CHEMICAL POLLUTANT RETENTION FROM AQUEOUS MEDIA

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Abstract. *Among the directions of capitalization of residual microbial biomass resulting in fermentation processes (biosynthesis or food industry), it can be considered its use in immobilized form in various natural polymers as a biosorbent for retaining chemical species polluting the aqueous environment. The aim of this study is to investigate the biosorption properties of immobilized residual microbial biomass by encapsulation in sodium alginate to retain the anionic reactive organic dye Brilliant Red HE-3B in a batch system of aqueous solutions. In order to evaluate the biosorption potential of the studied biomass, the influence of certain physical parameters such as temperature, pH of the solution, quantity and size of biosorbent particles, initial dye concentration and phase contact time were investigated. The obtained results confirmed that the biosorption capacity of the studied biomass increases with the temperature and the contact time of the phases until reaching an equilibrium, has high values in acidic environment due to the anionic character of the retained chemical species and depends on the amount of biosorbent used, particle size. Thus, it can be said that the studied residual biomass encapsulated in sodium alginate could be an efficient way to obtain new types of biosorbents with applicability in retaining textile organic dyes from industrial effluents before discharging them into sewage systems or recirculating them in different technological processes. In this sense, the study of biosorption processes can be complemented by modelling the biosorption equilibrium, thermodynamic and kinetic studies to establish the biosorption mechanism and identify the optimal conditions for the use of industrial processes.*

Keywords*: aqueous media, biosorption, dye retention, encapsulation, residual biomass.*

INTRODUCTION

Microorganisms are, in biochemical engineering, important sources for a large variety of intracellular and extracellular compounds such as: organic acids, amino acids, antibiotics [TORRES, 2020]. In these biosynthetic processes, the residual microbial biomass is an inevitable waste, generated in the separation step. These by-product microorganisms (bacteria, algae or fungi), could be used as a potential alternative to existing technologies for recovery of pollutants from industrial waste streams, due their ability to retain, by different mechanisms, pollutants from aqueous streams through biosorption [SUTEU et al., 2013; BLAGA et al., 2020; 2021].

Biosorption is a cost-effective, simple, passive accumulation process that includes different types of interactions: physical and/or chemical adsorption, ion exchange, coordination, complexation, or chelation. The microbial cell wall and the plasma membrane contain several functional groups (amino, carbonyl, carboxylic, phosphoryl, hydroxyl, phosphate, or sulphate groups) that are capable to bind pollutants [SUTEU et al., 2012; BLAGA et al., 2021; KANAMARLAPUDI et al., 2018]. The advantages of biosorption include: simplicity, no nutrient requirement for the non-living biomass, low sludge generation, low operational cost and high efficiency [SUTEU et al., 2012; REDHA, 2020; ELGARAHY et al., 2021].

Furthermore the use of free residual biomass can be significantly improved by immobilization: possibility for their use in continuous system, improved mechanical strength,

and easy biomass separation from the aqueous solution containing the pollutants [LOPES et al., 2017; RUSU et al., 2021a,b; SAHA and BHASKARA -RAO, 2021].

The use of microencapsulation (in natural polymers such as chitosan and alginate) for biomass immobilization is used for its advantages: improved stability, extended shelf life (storage time) and a large variety of particles shapes and sizes in accordance with the desired purpose [GAURI and SHIWANGI, 2017; LOPES et al., 2017; BLAGA et al., 2021].

The yeasts *Saccharomyces cerevisiae* and *pastorianus* are by-products in the production of alcoholic fermented drinks (wine and beer, respectively) and as a result, large quantities of residual yeast are available. Several studies have analysed *Saccharomyces cerevisiae's* capacity for accumulating heavy metals or dyes, due to its low safety risks and easiness in use [SUTEU et al., 2013; OJIMA et al., 2019].

The aim of this study is to investigate the biosorptive properties of microbial residual biomass of *Saccharomyces cerevisiae* and *Saccharomyces pastorianus* immobilized in sodium alginate for the retention of the reactive Brilliant Red HE-3B textile dye in a batch system from aqueous solutions. In order to evaluate the biomass's biosorptive potential, the influence of certain physical parameters such as temperature, pH solution, amount and particle size of biosorbent, dye concentration and phases contact time were investigated for batch biosorption process for Brilliant Red HE-3B. The obtained results suggest that the biosorbents obtained by encapsulating the residual biomass of *Saccharomyces cerevisiae* and *Saccharomyces pastorianus* have been shown to be effective in retaining organic dyes from aqueous media, environments in which they are present in moderate concentrations.

MATERIAL AND METHODS

Biosorbent. Two strains of yeast: *Saccharomyces cerevisiae* and *Saccharomyces pastorianus* separated from the fermentation broth and dried at 80°C for 4 hours in order to increase their biosorptive capacities) encapsulated in sodium alginate were used. For the encapsulation 1.5% low viscosity sodium alginate solution, prepared in distilled water at 70 °C was mixed with the residual biomass (5% d.w. concentration). BUCHI B390 microencapsulator was used, with the following conditions: the used nozzles diameters were 450 and 750 μm for *S. pastorianus* and 750 μm for *Saccharomyces cerevisiae*, air pressure 100 mbarri, T= 45°C, 500 V and 800 Hz (for 750 μm) and 200 Hz (for 450 μm). After complete homogenization the prepared suspension was dripped into 100mM calcium chloride (prepared in distilled water at 5 °C), through microencapsulator with selected nozzles, thus obtaining spherical beads with different diameter: Φ1 = 900 μm / Φ2 = 1500 μm.

Adsorbate. A reactive dye Brilliant Red HE-3B (BRed - C.I.25810; MW = 1463 g/moll, λ_{max} = 530 nm), was selected as organic chemical pollutant of aqueous system for this study. A stock solution (500 mg dye/L) using a commercial salty form of the dye with analytical reagent grade, and distilled water was prepared. For the experiments, solutions were prepared starting from the stock solution by appropriate dilution with distilled water.

All other necessary reagents were of analytical quality (p.a.), being purchased from the Chemical S.A. Company, Romania.

Biosorption methodology

The biosorption studies were performed in batch system, using 50 mL Erlenmeyer flask in which 0.2 g of encapsulated biomass (8 g/L with 5 % d.w.) and 25 mL of dye solutions were introduced. The solutions pH values were adjusted with 1N HCl and 1N NaOH solution. The constant desired temperature was assured by a thermostatic bath. The established working conditions were systematized in Table 1. After reaching the equilibrium time, the dye content in supernatant was determined spectrophotometrically using a JK-VS-721N VIS

Spectrophotometer at maximum dye wavelength (530 nm).

The biosorption capacity of the biosorbent representing the amount of retained dye by 1 g of biosorbent (q, mg/g), was calculated as follows:

$$q = \frac{C_0 - C}{G} \cdot V \quad (1)$$

where C_0 and C are the initial and the equilibrium dye concentration in solution (mg/L), G is the amount of biosorbent (d.w.) from alginate microcapsules (g) and V is the volume of dye solution (L).

RESULTS AND DISCUSSIONS

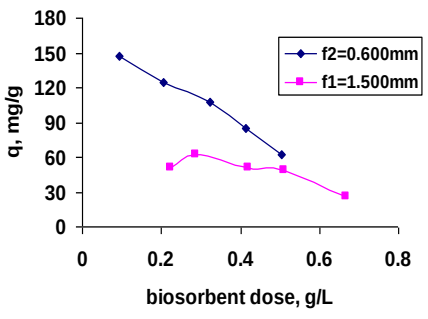
In order to appreciate the adsorptive properties of the obtained biosorbents, the biosorption capacity evolution in accordance to certain physical parameters involved in the process (solution pH, temperature of the process, dose of biosorbent, type of biomass, biosorbent microcapsules size, initial dye concentration, biosorption time) was studied. The variables studied and their limits of variation are presented in Table 1. In fact, they represent the conditions involved in the development of the biosorption process.

Table 1

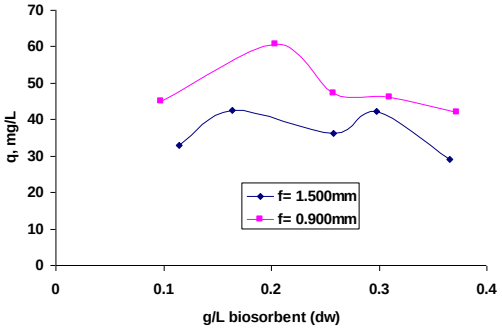
Physical-chemical parameters that influence the biosorption of Brilliant Red HE-3B dye onto biosorbent based on Saccharomyces cerevisiae and Saccharomyces pastorianus immobilized on sodium alginate

Parameters/ Studied limits of variation	**Type of biomass**	
	Saccharomyces cerevisiae	*Saccharomyces pastorianus*
pH	2	3
T, ^{0} C	25	5, 25, 45
t, hours	24, 48,72	24
Biosorbent dose, g/L with 5% d.w.	2.8	2.8-3.6 (depending on the microcapsules diameter)
Biosorbent particle diameter	1500 μm	900 μm; 1500 μm
Initial dye concentration in solution, mg/L	16.88 – 174.08	

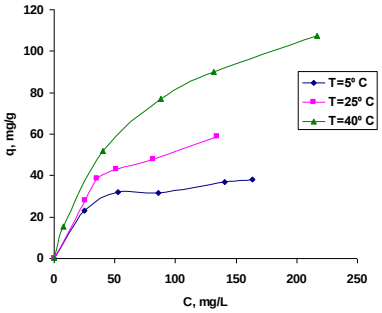
All the experimental results were systematized in Figure 1(a-g).



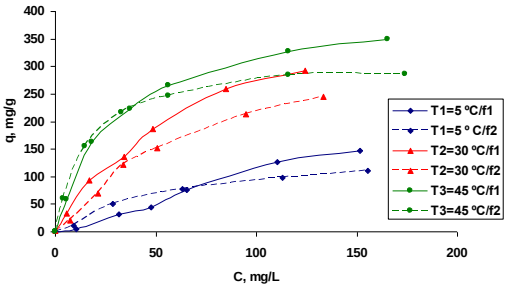
(a)



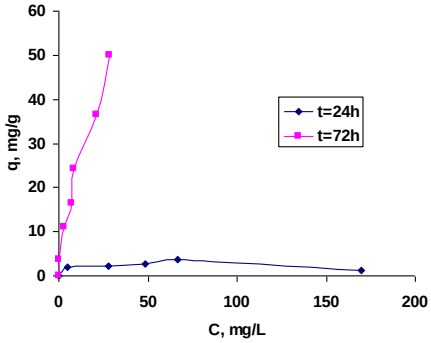
(b)



(c)



(d)



(e)

Fig. 1. Operating factors influencing the biosorption of reactive Brilliant Red HE-3B dye onto residual biomass of *Saccharomyces cerevisiae* and *Saccharomyces pastorianus* encapsulated in sodium alginate (biosorption capacity): (a-b) biosorbent dose and diameter size: *S. cerevisiae*- C_0 = 53.2mg/L; T=25^{0}C; pH=2; t=24h; ϕ1 = 1500μm; ϕ2 = 600μm; *S. pastorianus* - C_0 = 31.95mg/L; T=30^{0}C; pH=3; t=24h; ϕ1 =900 C_0 = 53.2mg/L; T=25^{0}C; pH=2; t=24h; ϕ = 1500μm; and ϕ2=1500μm; (c-d) temperature and initial dye concentration: *S. cerevisiae*- C_0 = 53.2mg/L; pH=23; t=24h; ϕ = 1500μm; biosorbent doze =2.4g/L; *S. pastorianus* - C_0 = 31.95mg/L; T=30^{0}C; pH=3; t=24h; ϕ1 =900; C_0 = 53.2mg/L; T=25^{0}C; pH=2; t=24h; ϕ = 900μm- biosorbent doze =2.8g/L; and ϕ2=1500μm- biosorbent doze =3.2g/L; (e) phases contact time and initial dye concentration: *S. cerevisiae*- C_0 = 53.2mg/L; pH=2; ϕ = 1500μm; biosorbent doze =2.4g/L

The biosorption process of the studied dye, using residual biomass encapsulated in sodium alginate, is dependent on a number of physical parameters (Figures 1 (a-g)), as follows:

- An important parameter is the *dye solution pH* that is brought into contact with the biosorbent. Its value determines the ionic form of the functional groups of the dye (especially sulphonic groups), but also the loading of the biosorbent surface, due to the ionisation possibilities of specific functional groups (-COOH, -OH, -NH_2, -SO_3, -CN, etc.). Being an anionic dye, its retention is influenced by the acid environment, the maximum biosorption capacity being obtained at the pH value of a strongly acidic media (pH=3), value being determined in our previous studies [NICA et al., 2021].
- Figure 1a+b show a decrease of the biosorption capacity as the amount of biosorbent increases for all three biosorbent particle sizes. The highest value of the biosorption capacity for the reactive Brilliant Red HE-3B dye was obtained in the case of biosorbent particles with a diameter of 900μm in the case of *S. pastorianus* biomass and 600μm in the case of *S.*

cerevisiae biomass. This behaviour is explained by the fact that the small particles provide a much larger contact surface between the phases which ensures a better contact between the phases which contributes to the more efficient retention of the Brilliant Red HE-3B dye.

- The biosorption process is favourably influenced by the *temperature* and the *initial dye concentration* (figure 1c + d). The increase of the adsorption capacity with the increase of the temperature is registered in the case of both types of biomass and, respectively in the case of both values of the diameter of the biosorbent particles (*S. pastorianus*), which suggests the possibility of an exothermic process. From these figures it is observed the increase of the biosorption capacity with the increase of the initial concentration of the dye until reaching a saturation point after which the capacity does not increase or increases extremely slowly. This can be explained by the saturation of the active centres of the biosorbent capable of binding the dye molecules. Also, in the case of *S. pastorianus* (figure 1d) the previous observation is confirmed, respectively the fact that in the case of the biosorbent present in the form of microcapsules with smaller size (900μm) the registered biosorption capacities are higher than in the case of granules with larger dimensions (1500μm).
- The biosorption capacity increases with the *contact time of the phases* (figure 1e + f), explained by the fact that active centres are gradually occupied until their saturation is reached. The increase occurs initially gradually and then slower so that in the end a plateau (equilibrium) is reached. The optimal time to reach equilibrium is approximately 6h (360min).

CONCLUSIONS

The removal study of reactive Brilliant Red HE-3B dye from aqueous solution using as biosorbent two residual yeast strains: *S. pastorianus* and *S. cerevisiae* encapsulated in sodium alginate, concluded that this types of biosorbents have adsorbent properties. Biosorption of this dye on the encapsulated residual biomass of *S. pastorianus* and *S. cerevisiae* depends on the initial solution pH (pH favourable value is 3), biosorbent dose (in range of 2.4.-3.2 g/L as a function of biomass microcapsules diameters), dye initial concentration (16.88 – 174.08 dye), phases contact time (> 400 min) and temperature (5°-40°C).

Obtaining this information and highlighting the existence of biosorbent properties of these biomaterials lead to the idea of the need for continuity thorough investigation of the biosorption balance to further expand the application of biosorbents based on encapsulated residual biomass to real industrial treatment systems.

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